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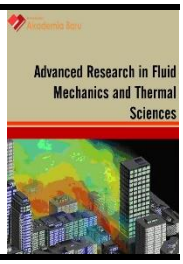

Thermal, Crystallinity and Microstructure Characteristics of Chemical Modification on Sugarcane Bagasse Powder

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ABSTRACT

The aim of this study was to evaluate thermal stability, crystallinity index, functional group and morphological characteristics of SCB fiber on chemical modification using sodium hydroxide (NaOH) and 3-aminopropyltrimethoxysilane (3-APS) treatment. The thermal stability, crystallinity index, functional group and morphological characteristics are analyzed using thermogravimetry analysis (TGA), x-ray diffraction (XRD) and scanning electron microscope (SEM) respectively. As a result, untreated SCB fiber, the thermal and crystallinity of chemical modification using NaOH and 3-APS silane on SCB showed the improvement. However, the 3-APS silane has better thermal stability and higher crystallinity index compare NaOH treatment. The thermal degradation of cellulose and lignin for 3-APS silane SCB fiber have increased by 31.17 °C compare to NaOH by 25.03 °C. Moreover, the crystallinity of silane fiber increases by 1.27 % compared to the NaOH only 1.12 %. From the morphology, the surface of untreated has impurity on the surface of SCB fiber. However, the NaOH treatment, the surface of SCB fiber become rough meanwhile the 3-APS silane SCB fiber, have smooth and cleaner surface.

1. Introduction

The sugarcane (Saccharum spp.) bagasse is a residue widely generated in high proportions in the agro-industry [1]. Bagasse is fiber mainly constituted by cellulose that is made of glucose with relatively high modulus, often found as a fibrillar component of many naturally occurring composites [2]. A fibrous residue of cane stalks left over after the crushing and extraction of juice from the sugarcane was called bagasse. Usually, sugarcane factories used this bagasse as fuel for the boilers [3]. However, excess baggage accumulation cause waste problem for the sugar industry [4]. The sugarcane bagasse may cause an effect on environment pollution such as land, water and air by means of leaching, dusting and volatilization.

Therefore, with suitable chemical modification on this fiber can be used to prepare lightweight composites and in many other applications. However, the hydrophilic nature of this cellulosic fiber

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limits their applications as it results in poor chemical as well as moisture absorption resistance [5]. The mechanical properties like tensile strength, hardness, and impact strength, thermal stability and water absorption can be improved using chemical modification technique [6–10]. Many studies on chemical modification or treatment had been carried out to remove the hydroxyl groups from lignin and cellulose to improve strength and fitness of fiber [11, 12].

The aim of this preliminary study is to evaluate thermal stability, crystallinity index, and morphological characteristics of SCB fiber on chemical modification using sodium hydroxide (NaOH) and 3-aminopropyltrimethoxysilane (3-APS) treatment.

2. Methodology

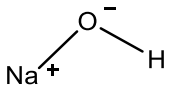
2.1 Material

Sodium hydroxide (NaOH) and 3-aminopropyltriethoxysilane (3-APS silane) were supplied by Alfa Aesar (M) Sdn Bhd. NBRr with particle size 300 – 150 µm was used in this research. The Sugarcane bagasse collected from Kilang Gula Felda Perlis Sdn. Bhd. Perlis, Malaysia contains 46.6 % of cellulose, hemicellulose 25.2 % and lignin 20.7 % by weight. The sugarcane bagasse was dried at 80 °C for 24 hours in the oven and grinded into 300 - 150 µm particle size prior to its usage.

2.2.1 Sodium Hydroxide (NaOH) Treatment

NaOH pellets and acetic anhydride were brought from Alfa Aesar (M) Sdn. Bhd. 5 % of NaOH pellets were mixed with 1000 ml of distilled water. 100 g of SCB was added into the NaOH aqueous solution and stirred for two (2) hours. After that, the SCB was rinsed with distilled water several times to remove the alkalinity. Next, 3 ml of acetic anhydride were added and mixed with the SCB powder followed by drying in the oven with a temperature of 60 °C for 48 hours. After 48 hours, the treated SCB were sieved to get a particular size of 150 - 300 µm. The chemical specification of NaOH used in this research shown in Table 1.

Table 1
The chemical specification of NaOH

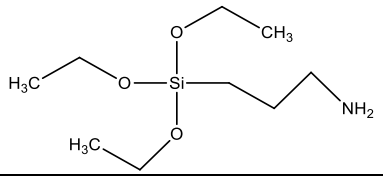
Properties	3-APS silane
Form	Solid
Appearance	White, waxy, opaque crystals
Molecular Weight	39.997 g/mol
Density	2.13 g/cm^3
Melting Point	318 °C
Chemical Structure	

2.2.2 Aminopropyltrimethoxysilane (3-APS) Treatment

Firstly, SCB fiber immersing in a mixture of water and ethanol (40/60 volume, respectively) and stirred for 1 hour at 60 °C. After that, the SCB was collected using a filter. 5 % of 3-aminopropyltrimethoxysilane was first introduced into 1000 ml of the mixture of water/ethanol and was allowed to stand for one hour. The pH of the solution was maintained at 4 with the addition of acetic acid. Then 100 g of SCB was added to the solution and the solution was continuously stirred for 1.5 hours. Then filtered and dried in the vacuum oven at 80 °C for 24 hours. All treated SCB

particles were crushed using a grinder to ensure the homogenous size of 150 – 300 µm. The specification and chemical structure of 3-APS silane used in this research shown in Table 2.

Table 2
The specification and chemical structure of 3-APS silane

Properties	3-APS silane
Form	Liquid
Appearance	Colorless or slightly yellowish clear liquid
Assay	99%
Molecular Weight	221.37 g/mol
Density	0.946 g/mL at 25 °C
Boiling Point	217 °C/760 mmHg
Chemical Structure	

2.3 Characterizations

2.3.1 Thermal analysis SCB fiber

Thermogravimetry Analysis (TGA) of the composites is carrying out with Perkin Elmer Pyris 6 TGA analyser. The sample's weight of about 15-16 mg is scanned at a heating rate 10 °C/min and from 30 °C to 500 °C. the scan is carried out using a nitrogen flowing rate of 50 ml/min. the continuous weight loss and temperature are analyzed to determine the following TGA indices (degradation temperature at 70 % weight, $T_{70\%}$ and final degradation temperature Tdeg of the composites) primary and secondary peak of DTG curve and thermal degradation.

2.3.2 X-ray diffraction (XRD)

The X-ray diffraction (XRD) spectra of the SCB fiber were recorded on Brucker D2 Phaser. The XRD is a type of powder X-ray diffraction. The x-ray tube is copper (Cu) type and generates at 30 kV and 10 mA. The diffraction machine was operated at a scan speed of 4° / min in steps of 0.05°. Eq. (1) shown the calculation of crystallinity index.

$$\text{Crystallinity Index, Cl (\%)} = (I_{002} - I_{am}) / I_{002} \times 100 \quad (1)$$

Where I_{002} was the maximum intensity of diffraction of the (002) lattice peak at a 2θ of 22-23° and I_{am} is the intensity of diffraction of the amorphous material, which was taken at a 2θ of 18° where the intensity is at a minimum.

2.3.3 Morphological properties

Studies on the morphology of the SCB powder were performed using a Scanning Electron Microscope (SEM). Scanning Electron Microscopy (SEM) Machine (FESEM ZEISS SUPRA36VP-24-58). The powder was coated with a thin platinum layer using Sputter Coater Polaron SC 515 to avoid electrostatic charging and poor image resolution during the examination.

3 Results

3.1 Thermal Analysis of SCB Fiber

Figure 1 and Figure 2 shows the Thermogravimetric Analysis (TGA) and Derivative Thermogravimetric Analysis (DTG) of untreated, NaOH treated, and 3-APS silane treated SCB. It can be clearly observed that all the SCB fiber underwent an initial weight loss between 50 and 110 °C related to the elimination of water and other primary volatile substances [13]. Based on Table 3, the temperature at 70 % of weight ($T_{70\%}$) and the char residual are recorded. The weight loss below 200 °C is negligible; above that temperature, the fiber begins to degrade fast and at 600 °C, only char residual is obtained due to loss of hydroxyl groups and depolymerization of cellulose. All the volatile materials are driven off from the sample resulting in the residual char [14].

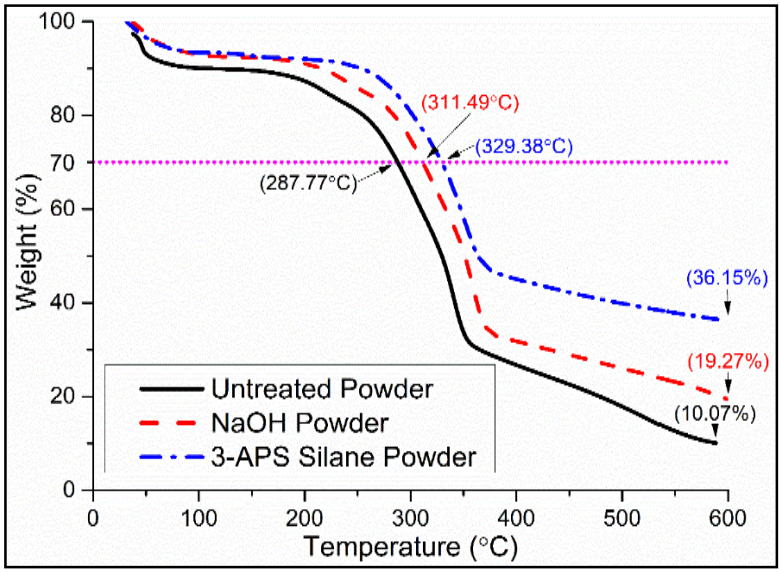


Fig. 1. TGA curve of untreated, NaOH and silane treated SCB fiber

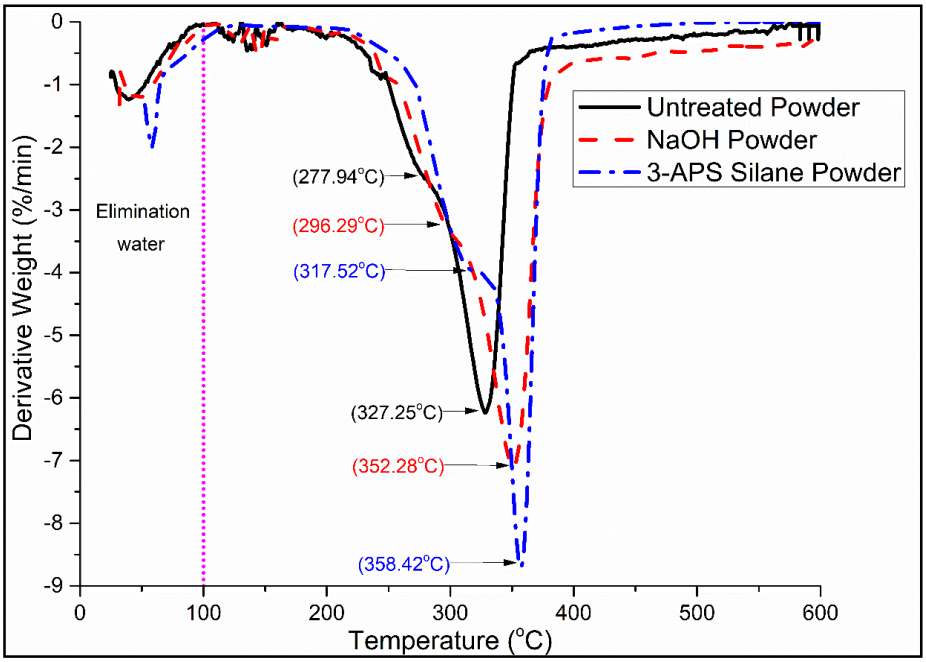


Fig. 2. DTG curve of untreated, NaOH and silane treated SCB fiber

The untreated fibre, the $T_{70\%}$ occurs at 287.41 ºC and the char residue is 10.07 %. Meanwhile, the NaOH treated SCB fiber, the temperature at 70 % of weight loss is 293.73 °C and 19.27 % of char residue. It was an increase of $T_{70\%}$ and char residue by 6.32 °C and 9.20 % compared to untreated SCB fiber respectively. Saha *et al.,* [15] reported in 'IR and X-ray diffraction studies of raw and chemically treated pineapple leaf fiber (PALF)' that alkali treatment reduces hemicellulose in the fibre, thereby making the fibre thermally more stable. Furthermore, Ray *et al.,* [16] also reported the increased thermal stability of alkali treated jute fibre in 'study of the thermal behavior of alkali-treated jute fibers'. However, the Silane-treated fiber, the T70% of weight loss is 329.20 °C and char residue is 36.15 %. The increase by 35.47 °C for $T_{70\%}$ and a higher percentage of the residue by 16.88 % compared to NaOH treated fiber, indicates better thermal stability of silane treated fibre compare to NaOH treatment.

Derivative Thermogravimetric Analysis (DTG) of untreated, NaOH treated, and 3-APS silane treated SCB. There are three (3) decomposition peaks. The first peak is for the remove of moisture content in fibers. It found in untreated, NaOH and Silane-treated SCB fiber at 37.2 °C, 43.85 °C and 58.22 °C respectively. The second peak is for the degradation of hemicellulose and the third peak for cellulose and lignin. However, the decomposition temperature of hemicellulose is lower in the case of untreated SCB fiber than in the cases of NaOH and silane treated fiber. The decompositions of cellulose and lignin of NaOH treated, and silane treated fiber is observed at 352.28 °C, and 358.42 °C respectively. This show the chemical modification have improved the thermal stability of fiber. Similar thermal decomposition patterns have been reported on other natural fibers [13,17,18]. However, the silane treatment better thermal stability compared to NaOH treatment.

Table 3
Thermal properties of SCB fiber

SCB fiber	Temperature at 70% weight, $T_{70\%}$ (°C)	Second peak (°C)	Third peak, T_{deg} (°C)	Char Residual %
Untreated	287.41	277.94	327.25	10.07
NaOH	293.73	296.29	352.28	19.27
3-APS Silane	329.20	317.52	358.42	36.15

3.2 X-ray Diffraction (XRD) of SCB Fiber

Table 4 and Figure 3 show the results of the X-ray diffraction analysis carried out to evaluate the crystallinity index of the untreated, NaOH and silane treatment of SCB fiber. The crystallinity index (CI) was calculated according to the Segal empirical method described in the experimental section as presented in Table 4. As seen from Figure 3, untreated SCB fiber exhibited typical cellulose I pattern, well-defended peak at 2θ = 22°. All samples presented the same diffraction pattern, with the highest peak in the 002 crystallographic planes representing the crystalline cellulose region [19]. Crystallinity is strongly influenced by biomass composition. The raw material presented the lowest relative crystallinity because it has a higher content of hemicellulose and lignin, which are amorphous [20]. The Crystallinity index of untreated, NaOH and silane treated are 42.84 %, 43.96 %, and 44.11% respectively. This increasing indicated the improvement in the cellulose structure and finally contributed to enhancing the tensile strength of the fiber.

Table 4
The crystallinity index of the untreated, NaOH and silane treatment of SCB fiber

SCB fiber	Maximum Intensity, $I_{(002)}$	Diffraction Intensity of amorphous, I_{am}	Crystallinity index, (CI) %
Untreated	3545	2026	42.84
NaOH	3792	2125	43.96
3-APS Silane	4216	2356	44.11

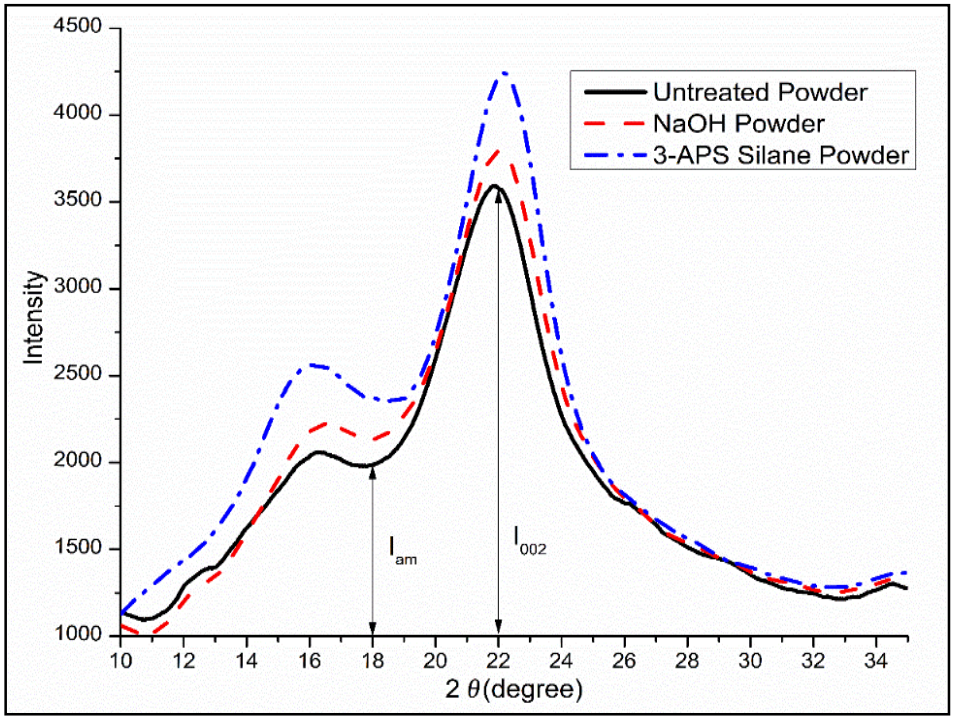


Fig. 3. Diffractograms of the untreated, NaOH and silane treatment of SCB fiber

3.3 Morphological Properties

Figure 4 shows SEM micrographs for untreated and treated SCB fiber. SEM examined the surface topology of untreated and treated SCB fiber is strong evidence that physical microstructural changes occurred at the fiber surface. After alkali treatment, fiber surface roughness was considerably increased and created fibers with smaller diameters probably due to the removal of hemicelluloses and lignin [21]. This rough surface facilitates both mechanical interlocking and bonding reaction due to the exposure of the hydroxyl groups to the matrix, thereby increasing the fiber–matrix adhesion [22]. According to Fernandes *et al.,* [23], the alkali treatment led to fibrillation of the sisal fiber bundles, reducing the diameter and increasing the roughness. Mwaikambo and Ansell [24] observed similar changes in the morphology of hemp, sisal and jute fibers after different alkali treatments. Joseph *et al.,* [25] observed by Scanning Electron Microscopy the fibrillation of banana fibers after the alkali treatment and they suggested that the removal of alkali-soluble hemicelluloses resulted in fibrillation of banana fibers. Meanwhile, the silane-treated fiber surface was smoother and cleaner than untreated fibers, which confirms that the surface of the fibers was modified by these treatments, and though surface features of fibers were not clearly visible, it seems to be an interlocked coating on its surface [26].

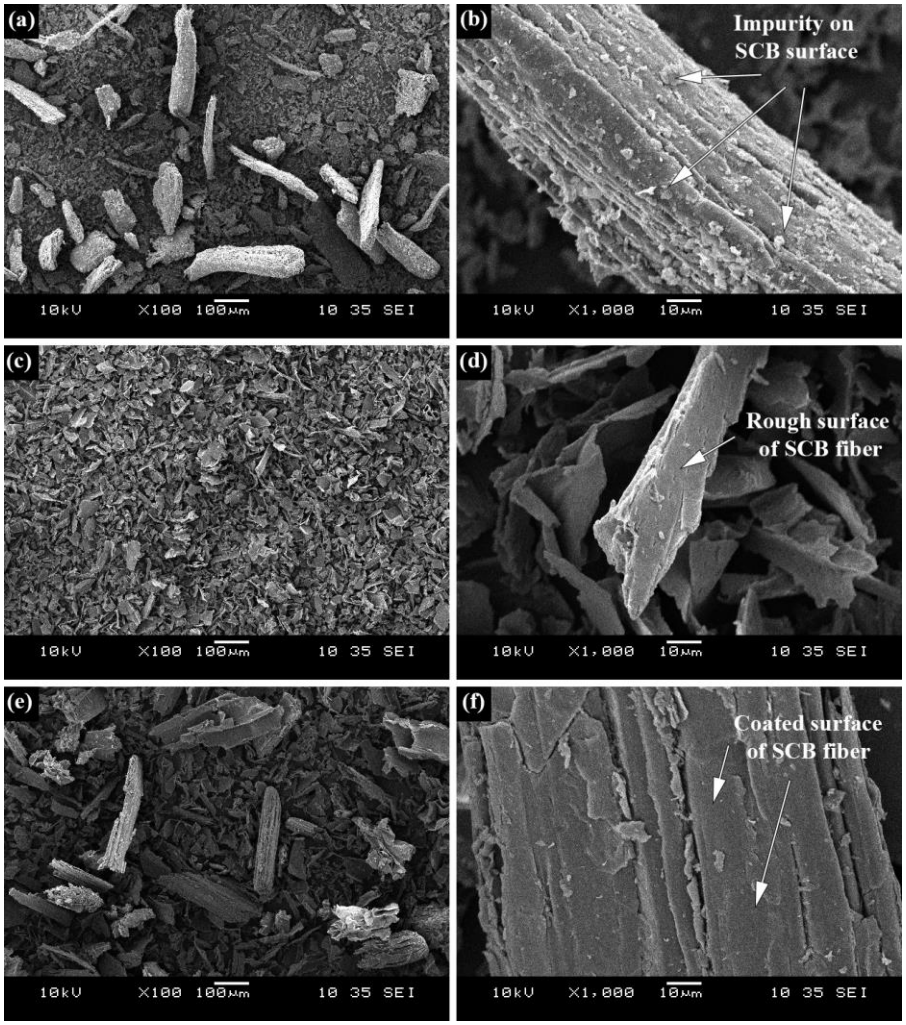


Fig. 4. SEM micrographs of the (a) 100x magnification and (b) 1000x magnification Untreated SCB fiber, (c) 100x magnification and (d) 1000x magnification NaOH treated SCB fiber, (e) 100x magnification and (f) 1000x magnification 3-APS treated SCB fiber

4. Conclusions

In this research shown comparison untreated and treated SCB fiber based on thermal and crystallinity of chemical modification using NaOH and 3-APS silane. Both treatments have shown the improvement in thermal properties and crystallinity index. However, the 3-APS silane has better thermal stability and higher crystallinity index compare NaOH treatment. The thermal degradation of cellulose and lignin for 3-APS silane SCB fiber have increased by 31.17 °C compare to NaOH by 25.03 °C. Moreover, the crystallinity of silane fiber increases by 1.27 % compared to the NaOH only 1.12 %. From the morphology, the surface of untreated has impurity on the surface of SCB fiber. However, the NaOH treatment, the surface of SCB fiber become rough meanwhile the 3-APS silane SCB fiber, have smooth and cleaner surface.

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